

# Biosorption of lead (II) from water using heartwood charcoal of *Areca catechu*: equilibrium and kinetics studies

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**Abstract** Present study was conducted to investigate the removal of Pb(II) from water by using heartwood charcoal of *Areca catechu* (HCAC). Batch experiments were conducted to determine the adsorption properties at different contact times (5–30 min), concentrations (0.1–10 mg/L), amounts of adsorbents (0.1–0.6 g), and in a range of pH 2–7. Most favorable biosorption condition was found at pH 5.0, 0.5 g biomass dosage and at 25 min equilibrium time. The experimental results were fitted to the Langmuir and Freundlich isotherm models; the Freundlich isotherm was found to well represent the measured sorption data implying HCAC has heterogeneous surface. Lagergren first-order and pseudo-second-order kinetic model were used to analyze the biosorption data; it was observed that the pseudo-second-order model best represented the relationship. Scanning electron microscopy image and energy dispersive X-ray analysis were also incorporated in support of the study. The result shows that HCAC has the potentiality to remove Pb(II) from water.

**Keywords** Biosorption · Lead (II) · Heartwood charcoal · Equilibrium study · Kinetic study

## Introduction

Natural or industrial pollution sources are mainly responsible for heavy metal contamination in different drinking water systems. Metal contamination is a major concern for their harmful effect in the environment. One of the most toxic heavy metals is lead and even in very low concentrations is detrimental to health. Important sources of heavy metal contamination urban industrial aerosols, solid wastes, mining activities, industrial, and agricultural chemicals are responsible for lead entering into the water supply of industrial and consumer utilities. Acid rain breaking down soils and rock, also releases heavy metals into streams, lakes and ground water (Hima et al. 2007). Lead is a cumulative poison and can elicit acute and chronic symptoms of poisoning. It is absorbed into bloodstream as it has high affinity for proteins, which leads to inhibition of the red blood cells. Its organic form is the fat soluble and has a tendency to drain into the brain. Due to the long half life in blood, soft tissues, and bones lead can cause anemia (Raziya et al. 2009; David et al. 2003). For removal of these metals from the environment, adsorption study has gained importance as concerned matter since the beginning of this century by various researchers. Adsorption of heavy metals goes along with a number of extremely important processes of effective significance. The technological, environmental and biological importance of adsorption is enormous because of its practical application (Dabrowski 2001). Several treatment technologies have been developed to remove lead from water and wastewater. Common methods include coagulation (Ogunfowokan et al. 2007), ion exchange, membrane separation, precipitation, electrochemical precipitation, microbiological processes (Valentina 2006), activated carbons, and biosorbents (Raziya et al. 2009). Different

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research studies shows that one of the most effective methods for the treatment of heavy metals from water is adsorption study using low-cost adsorbents. However no report on the utilization of HCAC, for biosorption of lead (II) has been found in literature. Influence of operating conditions like temperature, pH, biosorbent dose, and initial metal concentrations on the biosorption process were investigated in the present study. The equilibrium, kinetics, and thermodynamics of biosorption process were also studied.

## Materials and methods

### Charcoal preparation from heartwood

Heartwood of *Areca catechu* (betel-nut) plant was selected for this study. It was collected from Kamarpara village of Barpeta district (Assam, India). Initially heartwood was separated and washed with double distilled water followed by drying in the sun for 1 week. The material was then carbonized in a muffle furnace at about 100–200 °C for about 2 h. Finally, the carbon was crushed and sieved (425 µm) and stored in desiccators for further analysis.

### Preparation of metal ion solution

Metal ion solution was prepared from analytical grade chemical (Merck Ltd). Stock solution of 1,000 mg/L of Pb(II) was prepared from Pb(NO<sub>3</sub>)<sub>2</sub> in double distilled water. Few drops of 0.1 N HNO<sub>3</sub> were added to prevent precipitation of Pb(II). The working solutions were prepared from the stock solutions by diluting it to appropriate volumes. The initial pH of the working solution was adjusted to 5.0 by adding 0.1 N HNO<sub>3</sub> or 0.1 N NaOH solutions.

### Batch adsorption experiment

Batch sorption experiments were carried out at room temperature (30 ± 1 °C). Adsorption experiments were conducted at different conditions viz., contact time (5–35 min), pH (2–7), initial Pb(II) ion concentration (0.5–10 mg/L), and heartwood charcoal of *Areca catechu* (HCAC) dose (0.1–0.6 g). The adsorbent dose was maintained at 0.5 g/100 ml std. solution. The mixtures were taken in 250 ml conical flask and agitated on a mechanical shaker. The samples were filtered after analysis through whatman 40 filter paper. The concentrations of metals were determined by using atomic absorption spectrophotometer (Perkin Elmer AA 200) with flow injection analyzing mercury hydride generation system (Model FIAS-100) at 283.31 nm analytical wavelength. Experimental analysis was repeated

three times and the results were statistically analyzed. In the present work, adsorption could not be carried out beyond pH 7 due to precipitation of Pb(OH)<sub>2</sub> and therefore, the experiment were done in the pH range of 2–7.

The amount of adsorbed lead per unit mass of adsorbent ( $q_e$ ) was obtained using the following expression:

$$q_e = \frac{(C_o - C_e)V}{m}$$

whereas the amount of adsorbed lead per unit mass of adsorbent at time  $t$  ( $q_t$  mg/g) was obtained by using following expression:

$$q_t = \frac{(C_o - C_t)V}{m}$$

where  $V$  is the volume of solution treated in liter,  $C_o$  is the initial concentration of metal ion in mg/L,  $C_e$  is the equilibrium metal ion concentration in mg/L,  $C_t$  (mg/L) is the concentration of adsorbents at time  $t$ , and  $m$  is the biomass in gram.

### SEM and EDX analysis

The element analysis of HCAC before and after adsorption of Pb(II) is carried out by the energy dispersive X-ray (EDX) attached on the scanning electron microscopy (SEM, Leo, Model 1430VP) at Central Instrument Facility (CIF) department of Guwahati IIT, Assam.

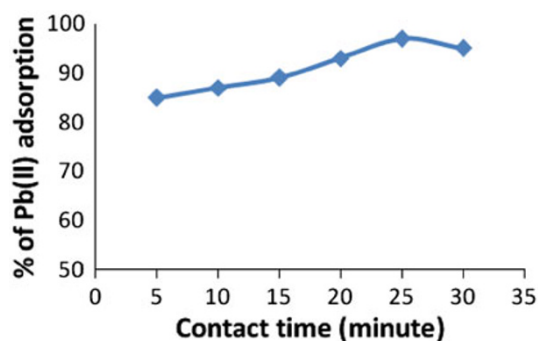
### FT-IR measurements

FT-IR spectra for both fresh and Pb(II) treated HCAC were obtained by KBr pellets methods operated on FT-IR spectrophotometer (Model- Bruker, Vector 22) to investigate the functional groups present in the charcoal and to look into possible Pb(II) binding sites.

## Results and discussion

### Effect of contact time

Effect of contact time on Pb(II) biosorption on HCAC is shown in Fig. 1. The absorption rate was fast initially for about 5 min (increase to 85 %) then later it increased slowly with respect to the contact time increases and finally reaches the equilibrium point at 25 min (increasing up to 97 %). Thus equilibrium time was considered to be 25 min, which was considered to be sufficient for the removal of Pb(II) ions by HCAC. The rate of percentage of metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals.



**Fig. 1** Effect of contact time on Pb(II) adsorption on HCAC; 100 ml single metal solution pH = 5.0, initial metal ion concentration ( $C_0$ ) = 1 mg/L, biosorbent amount = 0.5 g, and temperature = 30 °C

#### Effect of metal ion concentration

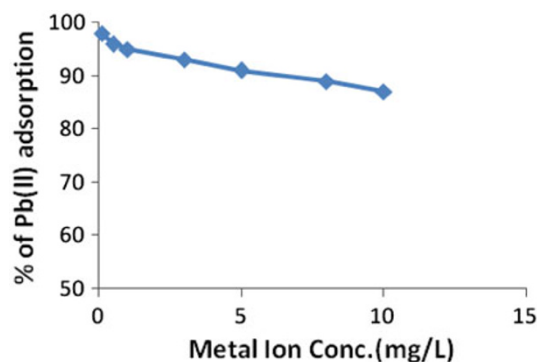
Effect of different metal solution concentration (0.1–10 mg/L) on the adsorption of Pb(II) ions by HCAC was shown in Fig. 2, where 0.5 g adsorbent dose was used. The efficiency of Pb(II) removal was affected by the initial concentration, with removal percentages decreases corresponding to increased in concentration. These effects may be due to presence of number of exchangeable sites in HCAC structure at low Pb(II)/HCAC ratios. As Pb(II)/HCAC ratio increases, exchangeable sites are saturated, resulting in a decrease in the adsorption efficiency (Guenay et al. 2007). As due to saturation of biosorption sites at higher concentrations, lower biosorption yield is observed. Therefore dilution of wastewaters containing high metal ion concentrations can increase the purification yield (King et al. 2008).

#### Effect of amount of adsorbents

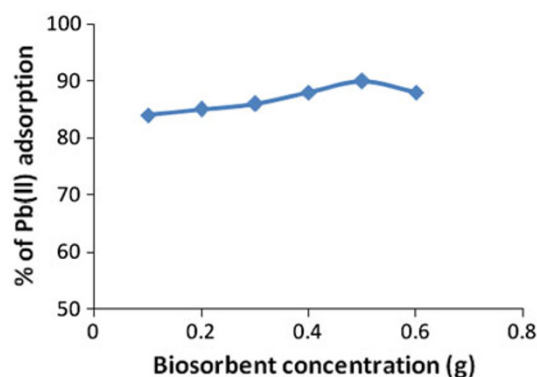
Figure 3 shows that extent of removal of Pb(II) increases as the amount of adsorbent increases from 0.1 to 0.5 g. The removal efficiency increases up to an optimum dose (0.5 g), beyond which the increase in removal efficiency is negligible for a given initial concentration. Similar cases are reported in removal of lead (II) using heartwood of *A. catechu* powder (Chakravarty et al. 2010). According to interpretations of similar data by Srividya and Mohanty (2009), “Higher uptake at low biosorbent concentration could be due to an increased metal to biosorbent ratio, which decreases upon an increase in dry biomass dose.”

#### Effect of pH

To establish the effect of pH on the biosorption of lead (II) ion, the batch equilibrium was studied at different pH values in the range of 2–7 (Fig. 4). The maximum removal of lead (II) ions was observed at pH 2–5 and slightly decreased at higher pH values. Similarly interpretations of



**Fig. 2** Effect of Pb(II) ion concentration on HCAC; initial metal ion concentration = 0.1, 0.5, 1, 3, 5, 8, and 10 mg/L; 100 ml of single metal solution; contact time = 25 min; amount of HPAC = 0.5 g; temperature = 30 °C, pH = 5.0

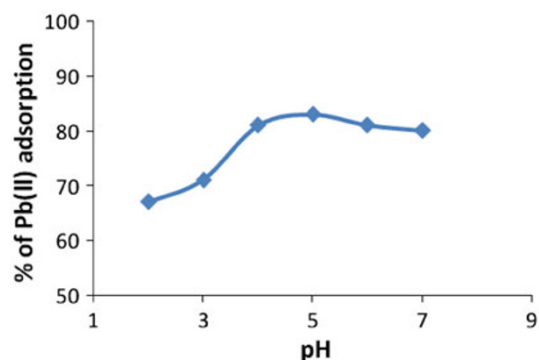


**Fig. 3** Effect of biosorbent concentration on Pb(II) on HCAC; 100 ml of single metal solution; contact time = 25 min, pH = 5.0; initial metal ion concentration = 1 mg/L, temperature = 30 °C

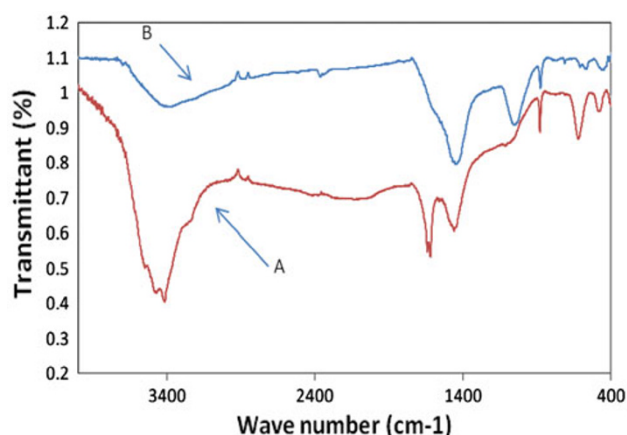
Reddy et al. are cited: “The main factors influencing the pH on biosorption process were Pb(II) species and surface functional groups on the adsorbents. It is generally known that at low pH values, concentration of  $H^+$  ions far exceeds that of the metal ions and hence  $H^+$  ions compete with Pb(II) ions for the surface of the adsorbent which would hinder the Pb(II) ions from reaching the binding sites of the adsorbent resulting in low adsorption amount of Pb(II). As the pH increases, there are fewer protons in the solution and consequently there is lesser competition with Pb(II) for binding sites. This results in the increase of the biosorption amount of Pb(II)” (Reddy et al. 2010).

#### FT-IR analysis

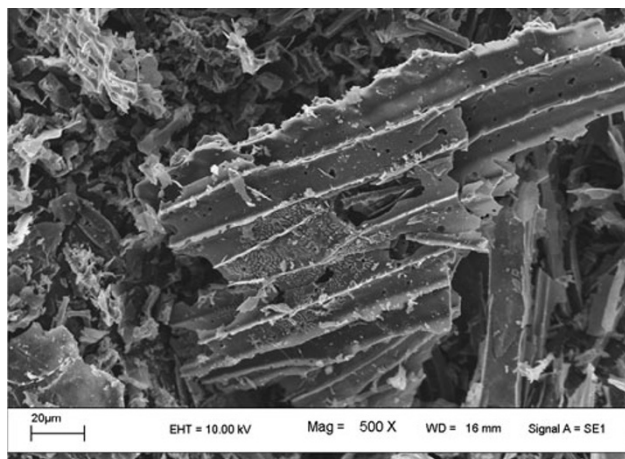
The FT-IR spectra of fresh and Pb(II) loaded HCAC shown in Fig. 5 were used to determine the vibrational frequency changes in the functional groups in the adsorbent. The spectra were measured within the range of 400–4,000  $cm^{-1}$  wave numbers. The spectra were plotted using the same scale on the transmittance axis before and after adsorption.



**Fig. 4** Effect of pH on Pb(II) adsorption on HCAC; 100 ml of single metal solution; contact time = 25 min, pH = 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0; initial metal ion concentration = 1 mg/L, amount of HCAC = 0.5 g, Temperature = 30 °C

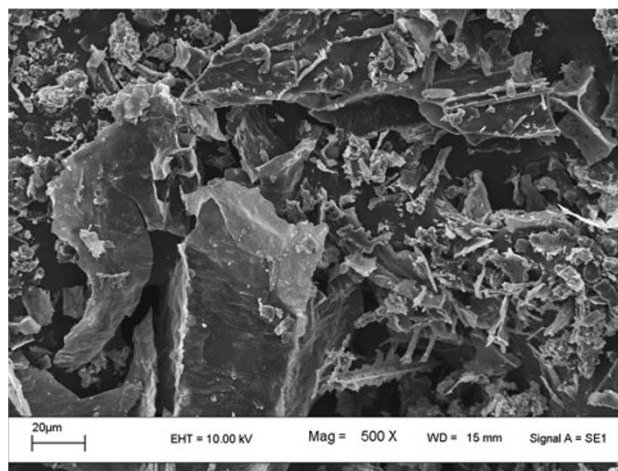


**Fig. 5** FT-IR spectra of fresh HCAC (A) and Pb(II) loaded HCAC (B)

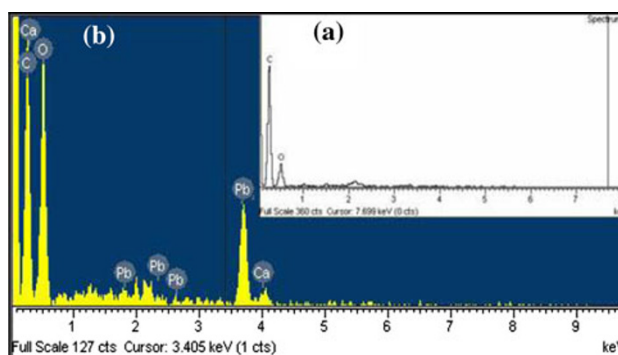


**Fig. 6** SEM micrograph of fresh HCAC

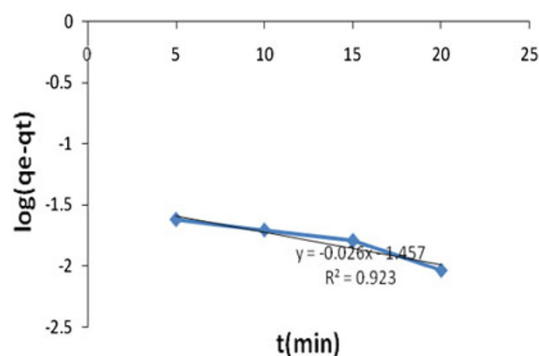
The FT-IR spectra of the adsorbent display a number of absorption peaks indicating the complex nature of studied adsorbent as shown in Fig. 5.



**Fig. 7** SEM micrograph of lead(II) loaded HCAC



**Fig. 8** EDX spectra of **a** fresh HCAC and **b** lead(II) loaded HCAC



**Fig. 9** Pseudo-first-order kinetic plot for the biosorption of Pb(II) by HCAC at 30 °C and pH 5.0

FT-IR spectrum of fresh HCAC shows peaks at 3,400–3,200  $\text{cm}^{-1}$  indicating the presence of –OH or –NH groups. A change in peak position (3,359  $\text{cm}^{-1}$ ) in the spectrum of the Pb(II) loaded biomass indicates the involvement of these groups in the biosorption of metal ion. The absorption peak at 2,861  $\text{cm}^{-1}$  could be assigned to –CH stretching vibrations of –CH<sub>3</sub> and –CH<sub>2</sub> functional



groups. The absorption peaks at  $1,616\text{ cm}^{-1}$  corresponded to the primary and secondary amide bands. Shifting of these peaks to  $1,587\text{ cm}^{-1}$  in metal loaded spectra, indicated involvement of these groups in metal binding. The peaks at  $1,442\text{ cm}^{-1}$  are attributed to symmetrical bending of  $\text{CH}_2$  group, asymmetric bending of  $\text{CH}_3$  and O–H bending. Shifting of these peaks to  $1,423\text{ cm}^{-1}$  indicates the participation of these groups in the adsorption process. The additional peaks at  $667.32$  and  $505.31\text{ cm}^{-1}$  can be assigned to bending modes of aromatic compounds. The shifts in the absorption peaks generally observed indicate the existence of a metal binding process taking place on the surface of HCAC.

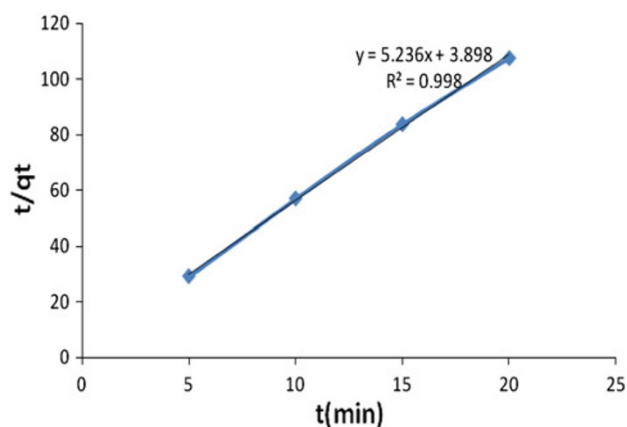
Figures 6 and 7 show fresh and lead loaded HCAC micrograph observed under SEM. Lead(II) loaded HCAC is brighter than the fresh one due to Pb(II) particles adsorbed by HCAC indicating the biosorption process. Analysis of microscopic images provides some interesting new opportunities for future research for establishing the relationship between particle surface textures and cellular responses (Gwynn and Wilson 2001). EDX was also carried out along with SEM, shown in Fig. 8a and b represents fresh HCAC and lead (II) loaded HCAC respectively. From the EDX analysis we can able to get elemental information of the material. A clear picture of lead(II) deposition was observed in Fig. 8a as HCAC was treated with lead(II) where as fresh HCAC has only few elements like C and O. Figure 8b revealed additional chromium signal, which conforms the binding of the metal ion to the surface of the biosorbent.

### Kinetic studies

For analyzing the adsorption kinetics of heavy metal ions, the pseudo-first and pseudo second order kinetic models were applied to experimental data. The first-order rate equation of Lagergren is represented as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}$$

where  $q_e$  and  $q_t$  are the amount of metal ion sorbed (mg/g) at equilibrium and at time  $t$ , respectively.  $K_1$  is the Lagergren rate constant of the biosorbent (1/min). A plot of  $\log(q_e - q_t)$  versus  $t$  gives the result shown in the Fig. 9. The value of  $K_1$  and  $q_e$ , calculated from the slope and intercept are presented in Table 1.



**Fig. 10** Pseudo-second order kinetic plot for the biosorption of Pb(II) by HCAC at 30 °C and pH 5.0

The following equation represents pseudo-second-order kinetic model (Lagergren 1898).

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

where  $q_e$  is the equilibrium biosorption capacity and  $K_2$  (g/mg min) is the pseudo-second-order rate constant. A plot of  $t/qt$  against  $t$  gives a linear relationship for the applicability of the second-order kinetic (Fig. 10).

Since the correlation co-efficient ( $R^2$ ) is 0.998 and the  $q_{\text{exp}}$  value is consistent with calculated one, the adsorption system studied could well be explained by pseudo-second-order kinetic model at all time intervals than the pseudo-first-order kinetic model ( $R^2 = 0.923$ ).

### Adsorption isotherms

Many sorption isotherm models are usually used to fit the adsorption isotherm data in order to obtain a linear regression data to predict the maximum adsorption capacity of the adsorbent. Langmuir and Freundlich models are the most widely used models in the case of the adsorption of metal ions with bioadsorbents (Fillipovic-Kovacevic et al. 2000).

#### Langmuir isotherm

For monolayer adsorption onto a surface containing a finite number of identical sites the Langmuir's isotherm model is valid. The Langmuir treatment is based on the assumption that a maximum adsorption corresponds to a saturated

**Table 1** Kinetic model parameters for the biosorption of Pb(II) by heartwood charcoal of *Areca catechu* (HCAC)

Pseudo-first-order parameters			Pseudo-second-order parameters			Experimental value
$q_e$ (mg/g)	$K_1$ (1/min)	$R^2$	$q_e$ (mg/g)	$K_2$ (g/mg min)	$R^2$	$q_e$ (mg/g)
0.0354	0.0113	0.923	0.19099	7.027	0.998	0.19526

monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface (Li et al. 2010). It can be expressed as follows:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e}$$

where  $q_e$  is the amount of metal ion bound to per gram of the biomass at equilibrium and  $C_e$  is the residual (equilibrium) metal ion concentration left in the solution after binding, respectively.  $q_{\max}$  is the maximum amount of metal ion per unit weight of sorbent to form a complete monolayer on the surface and  $b$  is the constant related to the affinity of the binding sites.  $q_{\max}$  and  $b$  can be determined from  $C_e/q_e$  versus  $C_e$  plot which gives a straight line of slope  $1/q_{\max}$  and intercept  $1/bq_{\max}$  (Aksu 2001).

Favorability of sorption of Pb(II) on HCAC was tested using the essential feature of the Langmuir isotherm, expressed in terms of a dimensionless constant,  $R_L$  (separation factor) which can be calculated as:

$$R_L = \frac{1}{1 + b C_0}$$

where  $b$  is the Langmuir constant and  $C_0$  is the initial concentration of metal ion. The value of  $R_L$  indicated the type of Langmuir isotherm to be.

$R_L > 1$  Unfavorable isotherm

$R_L = 1$  Linear isotherm

$R_L = 0$  Irreversible isotherm

$0 < R_L < 1$  Favorable isotherm

The  $R_L$  were found to be 0.8116–0.0413 for concentrations of 0.5–10 mg/L Pb(II) in the present work.

The equilibrium data obtained from the adsorption of Pb(II) onto HCAC were fitted to linear Langmuir equation (Table 2). Linear plot of  $C_e/q_e$  versus  $C_e$  (Fig. 11) was examined to determine  $b$  and  $q_{\max}$  values. The parameter indicates that the HCAC is a suitable ( $0 < R_L < 1$ ) adsorbent for the adsorption of Pb(II) from aqueous solution.

### Freundlich isotherm

Freundlich isotherm model is useful for multilayer sorption. Freundlich isotherm model for sorption of Pb(II) on HPAC is presented in Fig. 12. It can be presume from the model that metal ions removal take places on a heterogeneous adsorbent surface (Freundlich 1906).

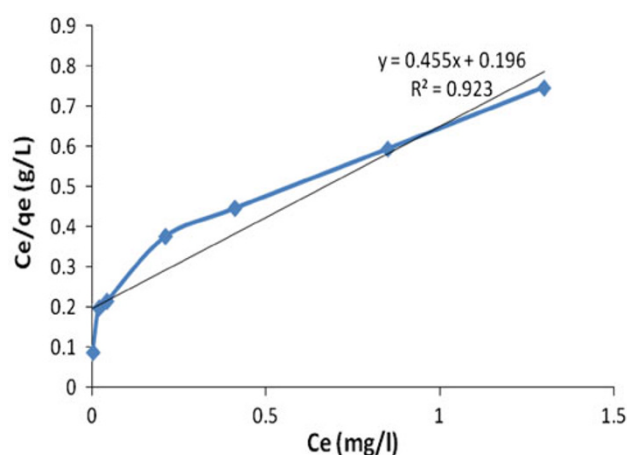


Fig. 11 Langmuir isotherm plot for Pb(II) adsorption onto HCAC

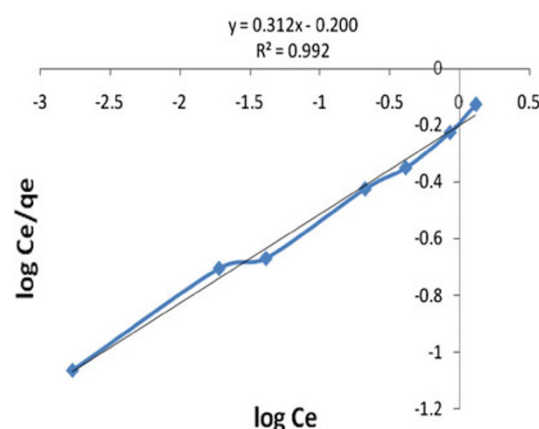


Fig. 12 Freundlich plot for Pb(II) adsorption onto HCAC

The Freundlich model is empirical in nature and is expressed as.

$$q_e = K_f C_e^{1/n}$$

where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  is the amount of metal ion bound to per gram of the biomass at equilibrium (mg/L), and  $K_f$  and  $n$  are the Freundlich constants related to the sorption capacity and sorption intensity of the sorbent, respectively. The equation can be linearised in logarithmic form and Freundlich constants can be evaluated by the following equation:

$$\log q_e = \log k + \left(\frac{1}{n}\right) \log C_e$$

**Table 2** Isotherm parameters for Pb(II) adsorption on heartwood charcoal of *Areca catechu* (HCAC)

Langmuir isotherm			Freundlich isotherm		
$b$ (L/mg)	$q_{\max}$ (mg/g)	$R^2$	$K_f$	$n$	$R^2$
2.321	2.198	0.923	0.6309	3.205	0.992

Table 2 shows isotherm parameters of HCAC. It is found that Freundlich isotherm models fit very well according to the correlation co-efficient values given in the table. Thus, the results of the present study indicate that biosorption of Pb(II) onto HCAC is heterogeneous in nature.

## Conclusion

In the present study, HCAC is established as to be an efficient removal agent of lead (II) from water. About 97 % removals was observed in case of 1 mg/L metal ion solution at pH 5.0 and at equilibrium time of 25 min. Similar finding are seen in the powdered heartwood of *A. catechu* experiment (Chakravarty et al. 2010). It is a low cost biadsorbent and available in different parts of the world. The kinetic study shows that pseudo-second order kinetic model is best fitted in the experiment which follows the first order rate equation and also provides a good fitting to the experimental data points. The adsorption isotherm study imply that Freundlich isotherm better explained the experimental data of Pb(II) biosorption by HCAC than Langmuir with correlation co-efficient 0.992. From the experiment therefore it can be concluded that HCAC can be used effectively as adsorbent for removal of Pb(II) from waste as well as from domestic water (as it shows very good result in case of very low concentration of 0.1 mg/l also).

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